

# Photochemistry of Polymeric Systems VII.\* Photo-cross-linking of Liquid Polysiloxanes Including Cinnamic Groups

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## Synopsis

Cinnamoyloxymethyl dimethyl vinyl silane was synthesized and bound to a series of commercial polydimethylsiloxane-type copolymers bearing variable amounts of Si—H functions through a hydrosilylation reaction. This reaction was controlled in order to avoid side reactions between the photosensitive unsaturated moiety and the Si—H groups.

The photosensitivity of polymeric films was studied by a photoresist test described in previous papers. The results emphasize the role of the molecular weight of the starting copolymer and the percentage of pendant photosensitive groups.

## INTRODUCTION

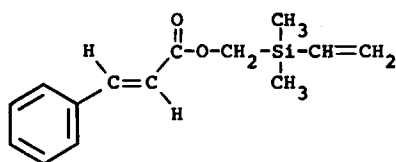
Ultraviolet (UV)-curable silicone polymers have been the subject of technical works and patents.<sup>2-8</sup> For example, polysiloxanes bearing triacrylic groups<sup>2</sup> can be used as liquid films, which harden in the presence of benzophenone when irradiated under UV light for a period of time shorter than 1 s. The photo-cross-linking of silicone polymers can be achieved from polysiloxanes bearing vinyl and mercapto end groups<sup>3</sup> or from cinnamic side groups, bound by hydrosilylation reaction of allyl cinnamate on a polysiloxane containing hydrogenosilane functions.<sup>4</sup> Some cinnamic derivatives have been introduced, too, using carboxylic esters.<sup>5</sup> Photosensitive polysiloxanes have been patented for many uses including cosmetics, paints additives, and varnishes.<sup>6-8</sup>

In this paper we report the synthesis and the photo-cross-linking properties of UV-sensitive liquid silicone polymers obtained from commercial poly(dimethylsiloxane)Co(methylhydrogenosiloxane) by hydrosilylation of cinnamoyloxymethyl dimethyl vinyl silane.

The photosensitive ester contains a terminal dimethyl vinyl silyl group that presents some important advantages with regard to the already reported syntheses: the selectivity of the hydrosilylation reaction is increased by the high reactivity of the vinyl silane function, and the presence of a  $\alpha,\beta$ -olefinic dimethylsilyl group does not allow the rearrangement of an allylic Pt complex during the metal-catalyzed functionalization.

\*See Ref. 1 for Part VI.

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Scheme I.

Furthermore, the photosensitive pendant groups are bound to the polysiloxane main chain by a flexible spacer nonsensitive to hydrolysis ( $\text{Si}-\text{CH}_2-\text{CH}_2-\text{Si}$ ), which is expected to afford good stability and compatibility to the resulting polymer.

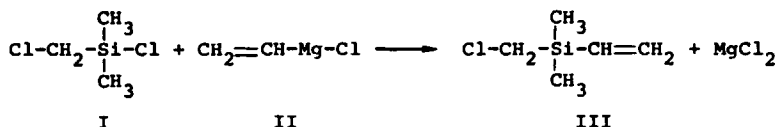
## EXPERIMENTAL

### Polymeric Samples

The polymeric samples were commercial poly(dimethylsiloxane)Co(methylhydrogenosiloxane), generous gifts from Wacker Chemie (oil 1562, SLM 71420) or from Rhone-Poulenc (oil 626, as well as (chloromethyl)dimethyl chlorosilane). The dynamic viscosity measurements of the starting and the modified polysiloxanes were performed at 25°C on a Heraeus Rotovisco RV 100 apparatus. The hydrogenosiloxane group content in the starting material was determined by hydrogen volumetry after reaction with alcoholic potassium hydroxide.

### Synthesis of the Photosensitive Group

The vinylic moiety of the photosensitive group III was synthesized by reacting (chloromethyl)dimethylchlorosilane I with vinyl magnesium chloride II:

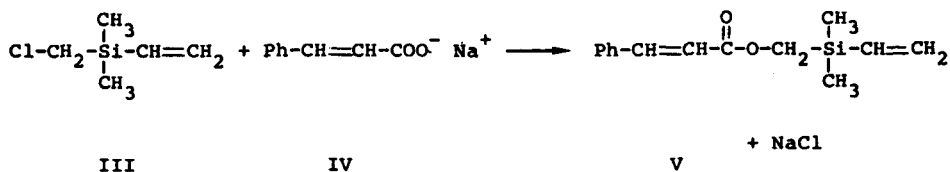


Scheme II.

Vinyl magnesium chloride was obtained by bubbling dry vinyl chloride (Sidercom, 99.95% purity) through tetrahydrofuran (THF) containing dry magnesium turnings. The reaction vessel was maintained for 6 h at 50°C and under nitrogen flow. The vinyl magnesium chloride yield was determined by Gilman's method.<sup>9,10</sup>

The freshly prepared THF solution of vinyl magnesium chloride, in small excess, was then slowly dropped into a solution of I in dry cyclohexane. The reaction mixture, kept below 20°C by external cooling, was stirred until completion of the reaction, treated with water, extracted, and filtered over celite. The solvents were then removed from the filtrate, which had previously been dried over magnesium sulfate. The silane III was recovered by distillation.

The photosensitive moiety was coupled to the vinyl silane III by nucleophilic substitution on the chloromethyl group by sodium cinnamate IV according to the following scheme:

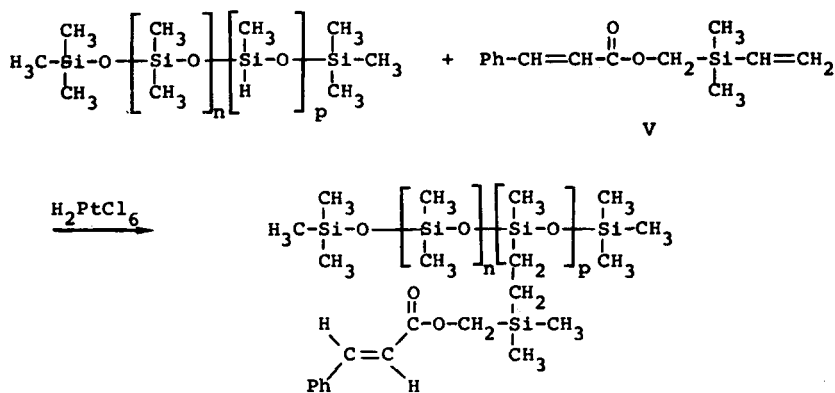


Scheme III.

This reaction, performed in *N*-methylpyrrolidone at a temperature of 120°C, was monitored by thin-layer chromatography (TLC) on silica gel (hexane-chloroform, 50/50 v/v). After 4 h of reaction, the solution was filtered and evaporated under reduced pressure. The residue was dissolved in diethyl ether and treated with an aqueous solution of ammonium chloride and then washed with water. The organic phase was then dried and concentrated. The photosensitive ester V was finally purified by distillation and characterized by elemental analysis, mass spectrometry, and UV, infrared (IR), and [<sup>1</sup>H] NMR (nuclear magnetic resonance) spectroscopy.

### Hydrosilylation Reaction

This reaction has been the object of a large amount of fundamental work and industrial applications; see, for example, the review of Lukevics.<sup>11</sup> Hexachloroplatinic acid H<sub>2</sub>PtCl<sub>6</sub> is the most common catalyst for the reaction. With V it can be written:



Scheme IV.

The hydrosilylation reaction was performed in thiophene-free toluene under a dry nitrogen flow and in a temperature range from 75 to 105°C. The catalyst was prepared as a stock 10<sup>-2</sup> M solution in isopropanol (Speier catalyst<sup>12</sup>) and was used in the reaction medium at a concentration of 10<sup>-4</sup> mol per hydro-

genosilane function. The reaction was carried out with an overall weight concentration of 50%. The extent of reaction was followed either by thin-layer chromatography or by the disappearance of the infrared Si—H vibration at  $2150\text{ cm}^{-1}$ .

#### Irradiation Methods: Photoresist Test

The preparation of thin films, their irradiation, the method of determining the amount of energy received by a given sample, and the bismuth photoresist test used for the determination of the insolubilization of the photoirradiated films are described in detail in Ref. 13.

Photosensitivity in this case is defined as

$$S = \frac{K}{E} = \frac{K}{I \cdot t}$$

where  $E$  is the energy needed to insolubilize  $1\text{ cm}^2$  of the film,  $I$  the illumination, and  $t$  the time needed for insolubilization.

The constant  $K$  is arbitrarily chosen as  $K = 1$ . This photosensitivity depends upon the source of irradiation.

All the photosensitizers that were used [xanthone, anthrone, benzanthrone, benzophenone, thioxanthone, Michler's ketone, pyrene, erythrosine, and BN (*N*-methyl-2-benzoyl- $\beta$ -naphthothiazoline)] were pure chemicals from Fluka, Aldrich, Merck, Prolabo, or Kodak. They were used at a weight concentration of 10% and were introduced into the solution of polymer before spreading the film.

Two series of photosensitivity measurements were performed under monochromatic light at  $\lambda = 280\text{ nm}$  (absorption maximum of the cinnamic chromophore) and in the absorption domain of the photosensitizer. The results were then compared to the sensitogram of the unsensitized polymer sample.

#### UV Kinetics

The disappearance of the absorption band of the cinnamic group at  $280\text{ nm}$  can be followed by UV spectroscopy as a function of the irradiation time. The rate of reaction  $\tau_r$  can be defined as

$$\tau_r = \frac{(\text{OD})_0 - (\text{OD})_t}{(\text{OD})_0 - (\text{OD})}$$

where  $(\text{OD})_0$  = optical density at  $\lambda$  max for time  $t = 0$

$(\text{OD})_t$  = optical density at time  $t$

$(\text{OD})$  = optical density corresponding to the residual absorption for the maximum time.

The variation in  $\tau_r$  can be drawn as a function of time. The optical densities were determined with a Cary 219 spectrophotometer.

## RESULTS AND DISCUSSION

### Polymeric Samples

The characteristics of the starting polysiloxanes are given in Table I. From these data were deduced the average number of siloxane units, which vary between 30 (oil 626) and 150 (oil SLM 1562).

TABLE I  
Characteristics of the Starting Polysiloxanes

Samples	$\bar{M}_n$	% Molar Si—H	Viscosity (mPa-s)
626	2200	16.9	30.7
1562	8000	21.1	87
SLM 71420	11000	11.9	167

TABLE II  
[<sup>1</sup>H] NMR Data for (Cinnamoyloxymethyl)Vinyldimethylsilane

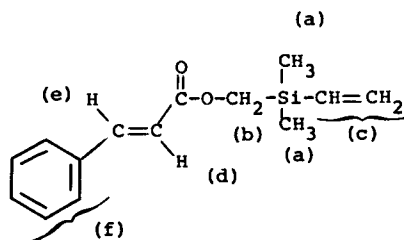
Chemical shifts (ppm)	Integration (multiplicity)	Assignment
0.15–0.20	6 (singlet)	(a)
3.95	2 (singlet)	(b)
5.5–6.2	3 (multiplet)	(c)
6.35	1 (doublet, $J = 16.5$ )	(d)
7.35	5 (multiplet)	(f)
7.6	1 (doublet, $J = 16.5$ )	(e)

### Synthesis of the Photosensitive Group

Vinyl magnesium chloride II was prepared with a yield from 80 to 100%. III was obtained by a final distillation  $T_{eb} = 119\text{--}122^\circ\text{C}$ . The characterization of III was made from IR and NMR spectra.<sup>4</sup>

The photosensitive group V was obtained by a final distillation under reduced pressure: ebullition,  $T_{0.1 \text{ torr}} = 100^\circ\text{C}$  (average yield 84% reported to III); elemental analysis, C (%) obtained, 68.29 (theoretical 68.25%); H (%) obtained, 7.38 (theoretical 7.36); and mass spectrometry, 246 ( $M^+$ , 0.4%), 245 (2.5%), and 131 (100%).

Table II lists the [<sup>1</sup>H] NMR characteristics in deuterated acetone. The assignment of peaks is given in this table following the notation



Scheme V.

The wavelength of the absorption maximum is 278.9 nm in chloroform. Beer's law is obeyed with  $\epsilon_{278.9} = 22,000 \text{ L mol}^{-1} \text{ cm}^{-1}$ .

Assuming that the value of  $\epsilon$  does not change appreciably when V is bound to the polymeric backbone, it is possible to use UV spectrophotometry to determine the percentage of photosensitive groups bound to polysiloxanes.



### Hydrosilylation Reaction

Preliminary experiments were carried out with oil 626 under stoichiometric conditions. Thin-layer chromatography and NMR spectra of the reaction products showed that a significant amount of photosensitive ester V was not reacted despite the complete disappearance of Si—H groups. The presence of free cinnamic ester in the final photosensitive material is not suitable since it could give rise, upon UV irradiation, to useless photocycloadditions with pendant cinnamic groups, which would decrease the practical photosensitivity of the photopolymer. Several attempts at purification by means of dialysis, precipitation, or distillation were unsuccessful or led to an important loss of polymeric material.

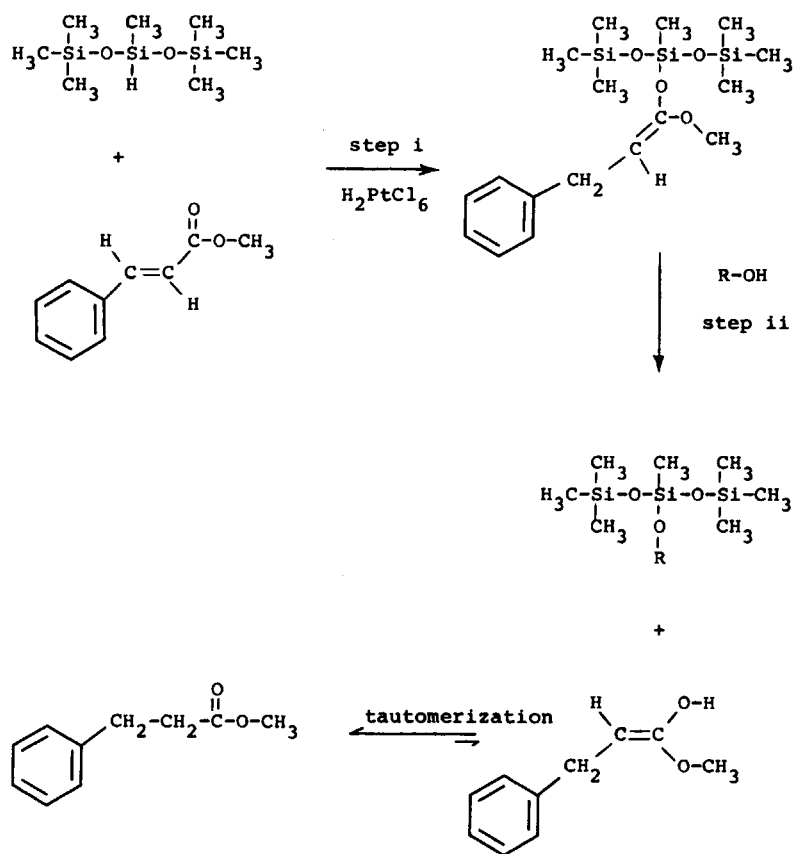
Hydrosilylation reactions were then carried out with an excess (10–15%) of hydrogenosilane groups with respect to the photosensitive vinylsilane V. [ $^1\text{H}$ ] NMR spectra of the resulting products showed the complete disappearance of both vinyl silane and hydrogenosilane functions; unexpected  $A_2B_2$  methylene signals can be observed in the 2.5–3.2 ppm range (Fig. 1), suggesting that side reactions involving the excess of Si—H groups occur during the course of the reaction. It is known that the addition of silicon hydrides on carbonyl compounds in the presence of transition metal catalysts is a convenient method to reduce a variety of organic functional groups.<sup>15,16</sup> We therefore suspected hydrosilylation of cinnamic groups to take place when the concentration of the more reactive vinyl silane falls under a critical value. This assumption was confirmed by experiments on model compounds. Methyl cinnamate was reacted with heptamethyl-1,1,1,2,3,3,3-trisiloxane in the presence of Speier catalyst yielding methyl phenyl-3-propanoate (75%), whose structure was established on the basis of spectroscopic data by comparison with an authenticated sample. The reduction of the cinnamic ester probably results from a two-step process:

1. 1,4 Addition of the hydrogenosiloxane on the  $\alpha,\beta$ -olefinic carbonyl group
2. Hydrolysis (or alcoholysis) of the intermediate silylenol ether and subsequent tautomerization.

This reaction takes place in the last stage of the functionalization of polysiloxanes and leads to interchain bridges (step 1), readily cleaved in the medium to give silanols and/or silyl ethers, together with pendant hydrogenated cinnamic esters (step 2), as shown in the NMR spectrum of Figure 1.

In order to avoid significant reduction of the cinnamic groups, 1,2-bis(diphenylphosphino)ethane was introduced in the reaction mixture as soon as free ester V could not be detected by TLC. The diphosphine, which displaces olefins from the platinum complex, acts as a poison preventing further hydrosilylation, and allows good shelf stability.

The characteristics of the polysiloxanes modified under these experimental conditions are reported in Table III. The effective molar ratio of cinnamic groups determined by UV spectrometry is about 5% lower than its theoretical value, except for polymer 626(12), which shows an important loss of chromophores (15%). The moderate dynamic viscosity of the different samples and their newtonian rheologic behavior allow solvent-free coating operations. The curves of Figure 2 emphasize the major role of the molecular weight on the increase in dynamic viscosity of the samples as a function of the percentage of photosensitive groups.



Scheme VI.

TABLE III  
Characterization of Modified Polysiloxanes

Starting polymers	Modified polymers	Molar % of SiH	Molar % of photosensitive groups		Viscosity at 25° C (mPa-s)	Physical aspect
			Maximum possible	Obtained		
626		16.9			30.7	Liquid
	626(12)		14	12.1	551	Liquid
	626(16)		16	15.9	827	Liquid
1562		21.1			87	Liquid
	1562(10)		10.6	10.0	920	Liquid
	1562(9.9)		10.6	9.9	815	Liquid
	1562(14)		15.0	14.0	2745	Liquid
SLM		11.9			167	Liquid
	SLM(6)		6.0	5.9	522	Liquid
	SLM(8.5)		8.9	8.7	1400	Liquid
	SLM(11)		11.3	11.0	2000	Mesomorphic?



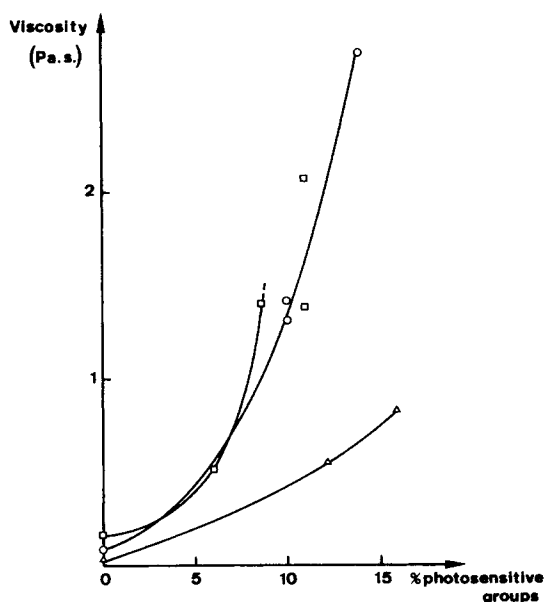


Fig. 2. Viscosity of modified polysiloxanes as a function of the molar percentage of photosensitive groups: 626 modified samples  $\Delta$ ; 1562 modified samples  $\circ$ ; SLM modified samples  $\square$ .

For high molecular weights (modified SLM polysiloxanes) and for a molar percentage of photosensitive groups of 11%, a special behavior appears. SLM(11) samples were transparent liquids after their preparation. After a few days, their viscosity increased strongly and they become opaque. However, they were always soluble in the usual solvents of polysiloxanes. This behavior might be the result of a mesomorphic organization of the polymers originating from the rather high percentage of carbon atoms in the long side chains, thermodynamically incompatible with the silicon backbone. Polysiloxanes with long carbon side chains have been recently shown to adopt mesomorphic structures.<sup>17,18</sup>

### Photochemical Study of Modified Polysiloxanes

At first some irradiations were performed with films obtained by evaporation of ethyl ether solutions on a solid support (glass, Teflon, and aluminum) in order to confirm the possibility of obtaining solid photoreticulated films. These tests were not satisfactory owing to the poor adhesion of the reticulated films on the support. The best results were obtained using water as the support: the liquid polymeric films prepared by evaporation of an ethyl ether solution at the surface of water were directly irradiated. The thickness of the reticulated films was approximately 15  $\mu\text{m}$ . The quality of the photoreticulated films depended drastically on the starting polymers:

1. Modified 626 samples gave scratched, brittle films with a rather important shrinking.
2. Modified 1562 samples gave a better result; the films were elastic and very little scratched.

TABLE IV  
Photosensitivity of Modified Polysiloxanes

Modified polymers	Molar % of photosensitive groups	$\bar{M}_n$	$S$ $\text{cm}^2 \text{J}^{-1}$
626(12)	12.1	3,185	4.11
626(16)	15.9	3,530	5.17
1562(9.9)	9.9	10,740	6.96
1562(10)	10.0	10,760	7.07
1562(14)	14.0	11,860	17.9
SLM(6)	5.9	13,220	3.47
SLM(8.5)	8.7	14,250	8.36
SLM(11)	11.0	15,120	9.97

3. Modified SLM(6) and SLM(8.5) gave very transparent unscratched films with a good elasticity. These first qualitative studies will be developed further in the laboratory. Up to now there is good conformation of the role of molecular weight.

#### Photoresist Test

This test was carried out on films spread on a polyester transparent support coated with metallic bismuth.<sup>13</sup> The developing solvent was chloroform and the time of development 1 min. Visualization was obtained by dissolving unprotected bismuth with a solution of ferric chloride (300 g/L).

The irradiation source was a xenon Hanovia L5430000, 900-W lamp. It was used in association with a Schoeffel monochromator. The wavelength was adjusted at the absorption maximum of the photosensitive group (280 nm) with a bandwidth of  $\Delta\lambda = 20$  nm

Table IV collects the results of the determination of photosensitivity  $S$ . The molecular weights of the modified samples are indicated. They were calculated

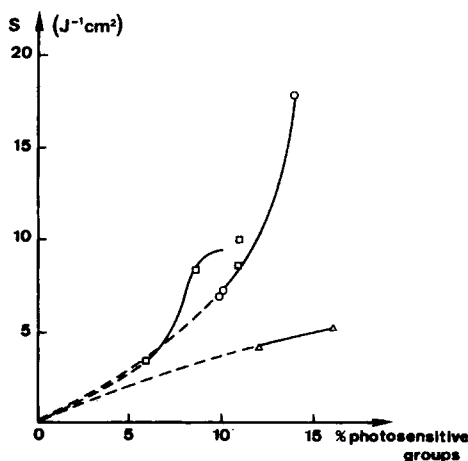


Fig. 3. Variation of the photosensitivity of modified polysiloxanes with their molar percentage of photosensitive groups: 626 modified samples  $\Delta$ ; 1562 modified samples  $\circ$ ; SLM modified samples  $\square$ .

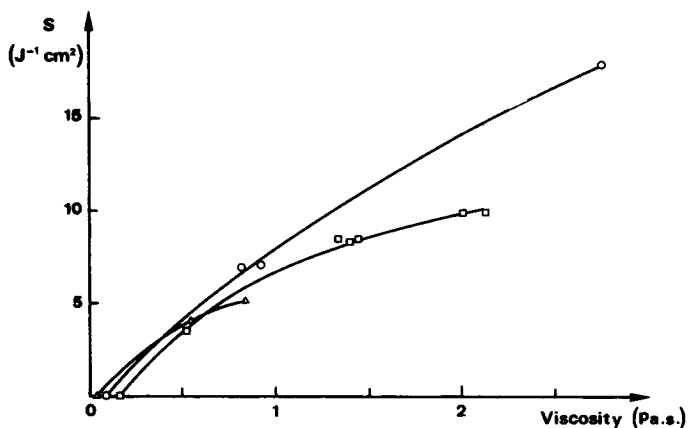


Fig. 4. Variation of the photosensitivity of modified polysiloxanes as a function of their viscosity: 626 modified samples  $\Delta$ ; 1562 modified samples  $\circ$ ; SLM modified samples  $\square$ .

from the percentage of modification and the percentage of Si—H groups given by the producer.

The importance of the molar percentage of photosensitive groups appears very clearly. It seems to be a more important parameter than the molecular weight itself. The reaction probability between photosensitive groups decreases drastically if their concentration is too low. If this concentration is 14% *M*, the photosensitivity jumps up to 17, as shown clearly in Figure 3. In Figure 4 the variation in *S* is given as a function of the viscosity of modified polymers.

The photosensitivity is of the same order of magnitude as that of Kodak KPR, which is a polyvinylcinnamate used with a large concentration of photosensitizers.

In order to increase the photosensitivity of our modified polysiloxanes, we tried different types of photosensitizers. Taking into account the triplet state energy  $E_T$  of the cinnamic group, which is approximately 50 kcal/mol,<sup>19</sup> various usual photosensitizers were tested under the different conditions described in Experimental.

Only pyrene and erythrosine exhibit a very small photosensitizing effect. Their triplet state energies  $E_T$  are 48 and 42 kcal/mol, respectively, that is, less than the triplet state energy of the cinnamic group. Moreover, usual photosensitizers, such as xanthone, anthrone, or benzanthrone, the triplet state energy of which is more than 70 kcal/mol, do not have any effect.

A possible explanation may be a thermodynamic microincompatibility between the hydrocarbon molecule of the sensitizer and the silicon backbone of the polymer.

#### *Kinetic Study*

Sample 626(16), a modified polymer with a high molar content of photosensitive groups, was chosen for kinetic studies. A thin film of the material was coated on a quartz plate and then irradiated for increasing times. It can be seen that, after 15 s, a very large amount of cinnamic double bonds are reacted. At this time the insolubilization of the film is already very well

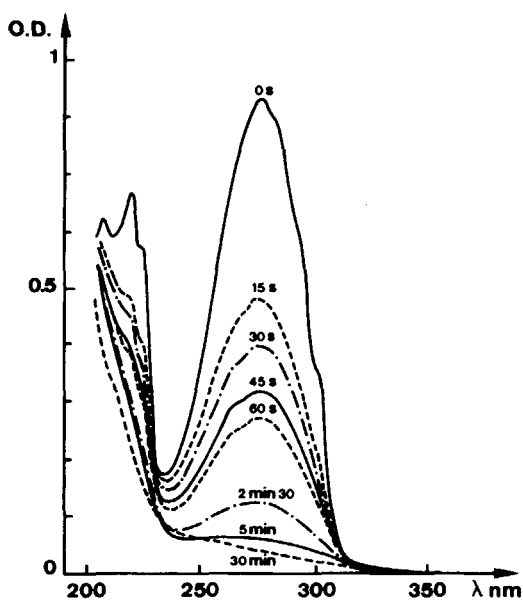


Fig. 5. Evolution with irradiation time of UV spectra of 626(16) modified polysiloxane.

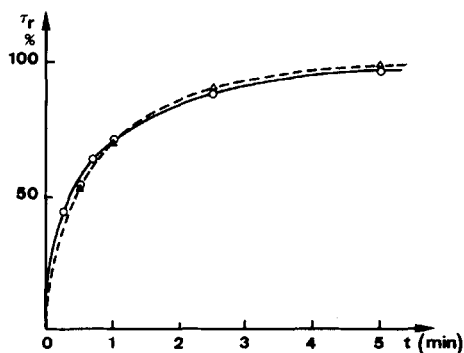


Fig. 6. Variation of the photoretication rate  $r$  as a function of time for 626 modified polysiloxanes: 626(12) modified samples  $\Delta$ ; 626(16) modified samples  $\circ$ .

achieved. Figure 5 describes the variation of the UV spectra with irradiation time for 626(16)-modified polysiloxane, and Figure 6 gives the corresponding variation in  $\tau_r$ .

## CONCLUSION

We succeeded in modifying hydrogenopolysiloxanes with cinnamic photosensitive groups. However, the hydrosilylation reaction must be very well controlled in order to avoid side reactions that decrease the photosensitivity of the obtained material. Photosensitivity was determined using a photoresist test. Unfortunately, photosensitivity cannot be improved by using conventional photosensitizers. However, the reported method allows the functionalization of polysiloxanes with more reactive photosensitive esters; studies are currently in progress in this direction.

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